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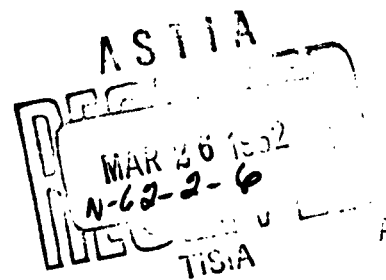# UNCLASSIFIED

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TECHNICAL FINAL REPORT

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RESEARCH ON IONISATION CHARACTERISTICS OF EASILY IONISABLE CHEMICALS

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A B S T R A C T

A laboratory method is outlined for studying some of the low energy ionic reactions that are likely to occur when easily ionisable chemicals are released into the ionosphere. The possibility of resolving some of the discrepancies in previous measurements of relevant cross-sections is discussed.

The design of apparatus to make measurements in afterglows using a time resolving mass spectrometer and a Langmuir probe is described, and the construction and initial measurements of performance of the mass spectrometer are given in detail.

C O N T E N T S

D I A G R A M S

1. INTRODUCTION

The work reported here has been concerned with constructing laboratory apparatus to study the ionic reaction occurring in a plasma under conditions similar to those existing in the ionosphere when a small quantity of an easily ionisable chemical is released.

Artificial electron clouds have been produced in the ionosphere by releasing easily ionisable chemicals from rockets fired to the appropriate heights. A general survey of this work has been given by Marmo, Dressman and Aschenbrand (1961). The chemicals used have been nitric oxide, potassium, sodium and caesium. The releases of caesium have been the most successful in producing clouds having a high electron population density and most of the work has been done with this material. By observing the peak ionisation level produced in these clouds and also by measuring the rate of decay of electron density it has been possible to deduce some information concerning the processes whereby ionisation is produced and lost in each case.

The ionisation processes which are most likely to occur in the release experiments are thermal ionisation and photoionisation of the contaminating chemical, although there is also a possibility that ionisation could be produced by excited gas particle impact. The electron loss processes which need to be considered are, firstly, direct recombination between electrons and positive ions, and secondly,

recombination via secondary processes such as charge transfer or electron attachment. It was decided to concentrate on some of the possible ionisation loss processes. These need to be studied at reacting particle energies similar to those found in the ionosphere (i.e., electron and ion energies in the range 0.04 to 0.2 eV.).

The most satisfactory method of studying reactions at such low energies is the afterglow method, which has been used by many observers to study diffusion, electron ion recombination and ion-ion recombination in a number of gases. One experiment which is of interest in this work is the measurement of electron-ion recombination coefficients in caesium. This has been carried out by two observers, Mohler (1937) and Dandurand and Holt (1951). In both cases the recombination coefficients were calculated from the observed decay of electron density as a function of time, in a caesium vapour afterglow, it being assumed that only one ion type was present. Their results may be summarised as follows :

Observer	Gas Pressure	Electron Temperature	Recombination Coefficient
Mohler	0.01 - 0.1 mm. Hg.	1200° K	3.4×10^{-10} cm.^{3}/sec.
Dandurand and Holt	0.32 - 0.68 mm. Hg.	Uncertain	3.5×10^{-7} to 1.2×10^{-6} cm.^{3}/sec. (varied with gas pressure)

The above measurements were made by two different methods :
Mohler measured electron density with probes, while the microwave
method originally developed by Biondi and Brown (1949) was used by
Dandurand and Holt. The results by the two methods are not in
agreement, nor do they agree with the theoretically expected value
of approximately 10^{-12}cm.^{3}/sec. for radiative recombination.
This suggests that there was more than one pr.ccss taking place
in both the above cases, and it is probable that these anomalies
can be cleared up if afterglow measurements are made in associa-
tion with mass spectrometer measurements. A mass spectrometer
for this purpose would need to have time resolution so that the
behaviour in time of any particular ion species occurring during the
afterglow period could be studied. This type of mass spectrometer
could also be used to study certain charge exchange reactions as
directly described by Dickinson and Sayers (1960). It was therefore
decided to build apparatus whereby it would be possible to study the
properties of the ions of easily ionisable chemicals by means of
afterglow techniques using a mass spectrometer.

2. METHOD

When setting up an afterglow experiment, it is necessary to consider
the means of producing the required initial high ionisation density in
relation to the proposed measuring techniques. It was decided
that it would not be possible to use a mass spectrometer under
afterglow conditions to measure absolute values of ion density
accuractly, and it is therefore necessary to include some means of
measuring the electron density in the afterglow. There are two

such methods which have been used satisfactorily in afterglows:
the standard microwave method, and the Langmuir probe method.
Both techniques have their advantages and disadvantages, but it was
decided that it would be simpler to use a Langmuir probe in conjunc-
tion with a mass spectrometer rather than to attempt to build a
spectrometer into a microwave system. A further decisive factor
was that the authors have had considerable previous experience of
probe measurements in afterglows. There is also a secondary
advantage of this arrangement over microwave measurements in
that there is no limit to the size of discharge vessel which may be
used. All laboratory measurements of this type suffer, to a certain
extent, from errors due to wall effects, such as wall recombination,
which leads to ionisation loss by diffusion as well as by the process
being studied. This effect can be minimised by using as large a
discharge vessel as practically possible. The diffusion loss is also
a function of gas pressure in the afterglow, and it can be supressed
by using sufficiently high gas pressures.

The most convenient method of producing a high and uniform ionisa-
tion density in a gas is by means of an R.F. discharge. It may be
shown that the rate of loss of ionisation by diffusion is proportional
to the ionisation density, while the rate of loss by volume recombina-
tion is proportional to the ion density squared. Therefore,
recombination can be emphasised at the expense of diffusion by having
as high an initial ionisation density as possible. This entails having
a very high powered radio-frequency ionising pulse which, however,
need only last for a sufficient length of time to ensure that the
ionisation density builds up to its maximum value. It is, therefore,
possible to use an oscillator which has a very moderate mean power
rating but which is capable of producing a very high peak pulse power.

Again, in order to keep diffusion effects small it is necessary to make the initial ionisation density distribution as uniform as possible, and this necessitates the use of the lowest frequency consistent with obtaining maximum power transfer to the gas.

Easily ionisable chemicals, in particular the alkali metals, are usually very reactive and hence it is necessary to design the mass spectrometer and vacuum system of materials resistant to attack by these chemicals. It is necessary for the mass spectrometer to be bakeable to obtain a good vacuum and hence high purity gas conditions. It will also be necessary occasionally to heat the discharge tube and mass spectrometer to obtain a suitable working vapour pressure of the contaminant, whose room temperature vapour pressure is too low. This facility will also enable the cross-sections of ionic reactions to be studied as a function of ion energy.

3. APPARATUS

The pulsed discharge necessary to form an afterglow is produced in a cylindrical Kodial glass discharge tube, with the mass spectrometer contained in a side arm. The Langmuir probe will also be in a side arm and will be arranged so that it may be moved radially across the tube, if necessary. The metal parts of the mass spectrometer and all lead out seals are made of Nilo-K alloy, which is a special glass sealing alloy having the same coefficient of expansion as Kodial glass over a considerable range of temperatures. This arrangement considerably simplified the

P = PIRANI GAUGE
T = LIQUID NITROGEN TRAP.

GAS BOTTLES

Ne

N₂

TAP C

TAP D

P

TAP B

C

KODIAL GLASS
PYREX GLASS

ABOVE THE LINE
THE SYSTEM IS
BAKEABLE

GRADED SEAL

T

P

I

IONISATION GAUGE

M°LEOD GAUGE

M

CIRCULATING DIFFUSION PUMP

TAP A

T

T

T

EVACUATING DIFFUSION PUMP

TO BACKING PUMP

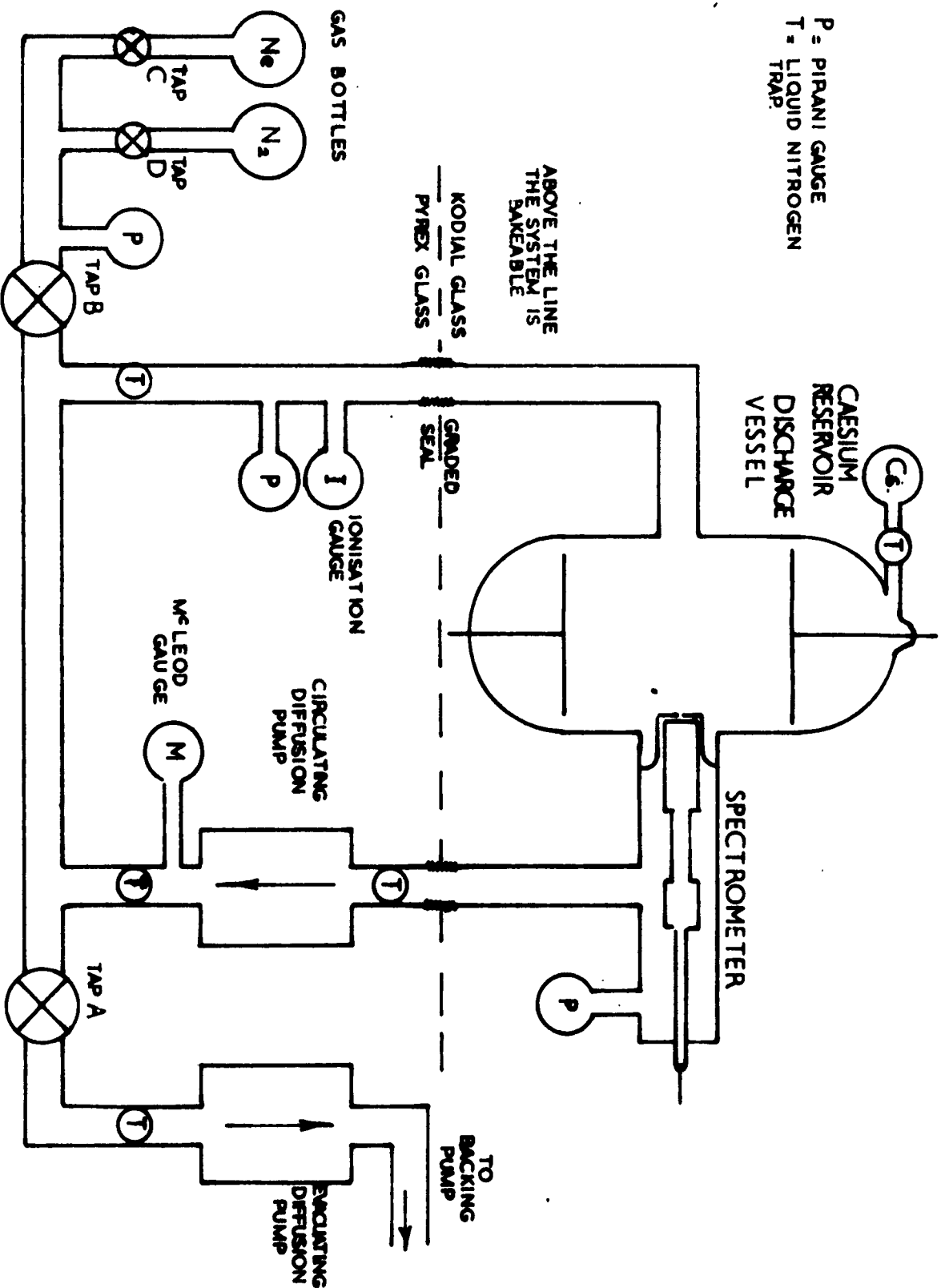CAESIUM RESERVOIR
DISCHARGE VESSEL

Cs

T

SPECTROMETER

P

DIAGRAM I. BLOCK DIAGRAM OF VACUUM SYSTEM

construction of the mass spectrometer as it was n. necessary to make allowances for differences in expansion during bake-out. Nilo-K is a nickel iron alloy, and so it is not strongly attacked by the alkali metal vapours or by mercury and hence the metallic parts are all - as far as possible - constructed of this material. The probe has not as yet been included in the system as its associated measuring equipment is still under construction. The various components of the apparatus will now be considered in detail under three separate headings.

3.1 The Discharge Tube and Vacuum System

A block diagram of the discharge tube and vacuum system is shown in diagram 1. The tube itself has an active volume approximately 16 cms. long and 16 cms. diameter. It contains two nickel disc electrodes which can be used as plasma reference electrodes, and also as a means of feeding in the power. It is necessary that these electrodes can be heated for cleaning purposes, and this will be done with an induction heater. In order to ensure that this heating is uniform a series of radial slots were cut in the discs. The orifice of the mass spectrometer is pierced in the centre of a 2.5 cm. diameter Nilo-K disc which is approximately $\frac{1}{2}$ cm. radially inwards from the wall of the discharge tube. This disc is sealed into the end of the glass tube which forms the side arm containing the mass spectrometer. The vacuum system has two separate parts, firstly the evacuating and gas filling system, and secondly a circulating pump which returns the gas leaking through the spectrometer orifice to the discharge tube and maintains a low pressure in the spectrometer

itself. The discharge tube and mass spectrometer side arm are
made of Kodial glass while the rest of the vacuum system is made
of Pyrex glass to enable certain commercial Pyrex components
to be used. The two types of glass are joined by means of graded
seals. The two taps which seal off the discharge tube from the
evacuating and filling lines (A and B respectively) are both of all-
stainless steel construction, apart from the flange sealing washers
which are copper. It was found that these washers could be given
a thin coating of nickel to prevent attack by mercury without impair-
ing their sealing qualities. The other two taps (C and D) are of all
metal construction but contain copper; this is not of great impor-
tance as they need not come into direct contact with either mercury
or the alkali metal vapours. Mercury pumps are used, since if
mercury occurs as an impurity it can easily be identified with the
mass spectrometer. The use of oil pumps, particularly for the
circulating pump, is not desirable since any hydrocarbon vapours
entering the discharge tube would be decomposed into impurities
which might not be removed by the liquid air traps.

The evacuating pump is a commercial two-stage diffusion pump of
glass construction, while the circulating pump also is constructed
of glass but has three-stages of special design. The circulating
pump has an unbaffled speed of 70 litres/sec. and it is capable of
working into a backing pressure of 5 mm. Hg. Both the pumps
have liquid air traps and there are two traps in series between the
low pressure end of the circulating pump and the discharge tube.

Accurate pressure measurements are made with a McLeod gauge
which covers a pressure range from 100 mm. Hg. to 10^{-4} mm. Hg.
Three Pirani gauges are included to provide a continuous monitor

of the pressure in various parts of the system. These gauges were
made specially for the purpose as there are no commercial glass
gauge heads available which can be baked. A suitable Pirani gauge
control unit was also designed and made to work in conjunction with
these heads, the pressure range covered being 0.2 mm. Hg. to
10^{-4} mm. Hg. An ionisation gauge is also included to measure
the ultimate pressure attainable in the discharge tube. The dis-
charge tube and mass spectrometer are arranged so that they can
be even baked. The high vacuum taps all have built in heaters
while the rest of the system, apart from the diffusion pumps, can
be baked if necessary by means of heating tapes.

No part of the vacuum system has as yet been baked and the best
ultimate pressure attained so far has been 10^{-6} mm. Hg. The
maximum pressure which can exist in the spectrometer for it to
perform satisfactorily is 10^{-3} mm. Hg. and this has been found to
be maintained with discharge tube pressures up to 2 mm. Hg.
The alkali metal vapours can be introduced directly into the dis-
charge by evaporation from a side arm connected to one end of
the discharge tube.

3.2 The Pulsed R.F. Power Supply

It has been found from previous experience that an oscillator fre-
quency of approximately 7 Mc/s gave the most uniform initial ionisa-
tion density distribution, and higher frequencies were found to
give a 'hollow' plasma, due to skin effect. The oscillator is the
standard cross coupled push pull arrangement, having a maximum

mean power rating of 100 watts and it has a continuously variable output impedance over the range 15 to 700 ohms. The anodes of the oscillator valves are fed from a pulse modulator, which gives pulses of 200 μ secs. duration at a repetition frequency of 50 C/s synchronised to the supply mains frequency. The power available is variable up to a maximum peak pulse power of 100 Kw. The output of the oscillator is at D.C. earth potential, so the power is fed to the discharge tube via a coaxial isolating transformer, which makes it possible to have the discharge tube electrodes at a D.C. potential with respect to earth when necessary.
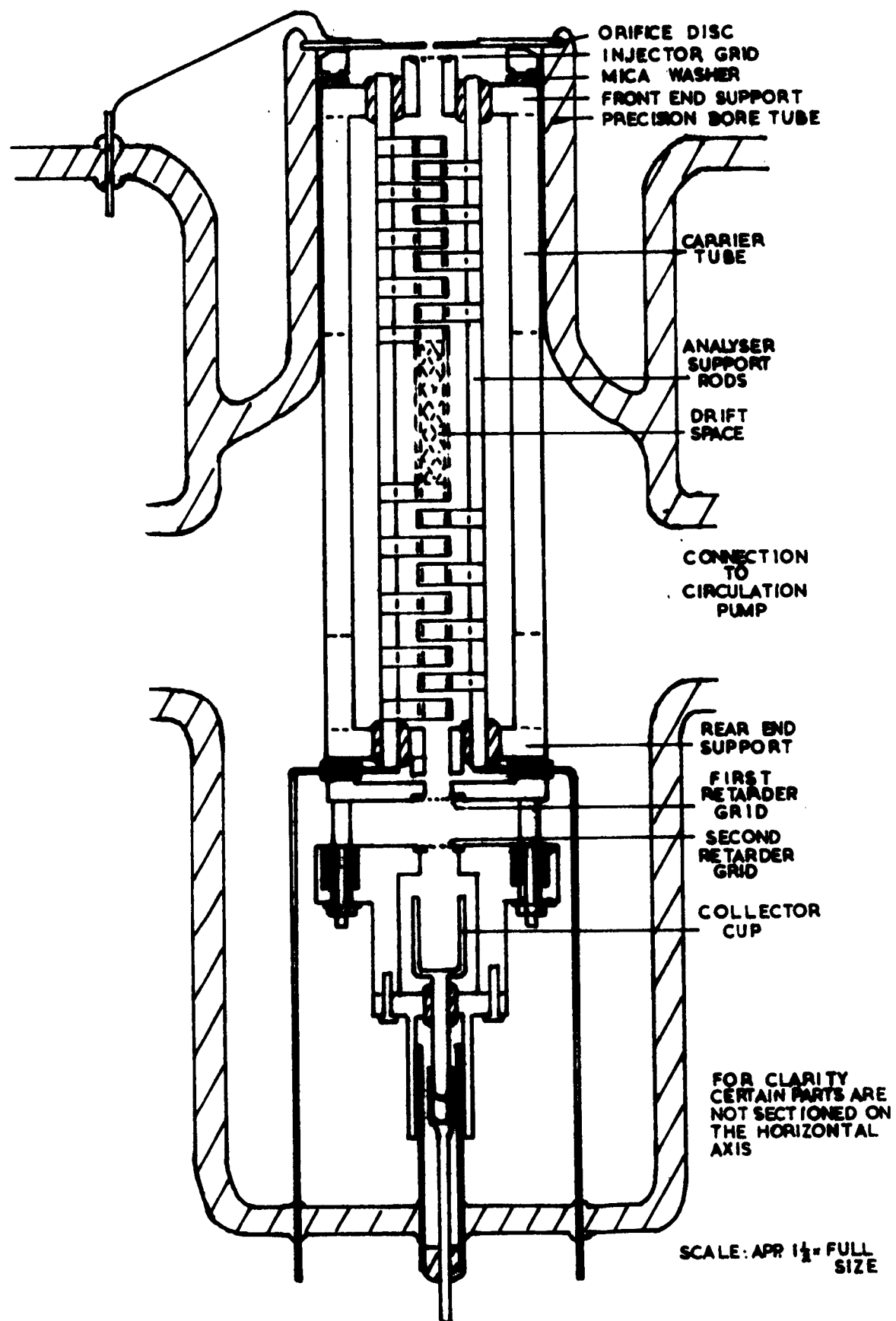
3.3   The Mass Spectrometer

A mass spectrometer suitable for making the required measurements in afterglows must fulfil a number of conditions:

a)   It must disturb the afterglow conditions as little as possible:

b)   It must be capable of working with a discharge tube pressures of the order of 1 mm. Hg.

c)   It must have sufficient resolving power to separate the expected ion types. The most critical ions in this respect are probably those having masses of 28, 30 and 32 a.m.u.

d)   The ion collection and measuring arrangement must have a large enough bandwidth to avoid distortions of the observed ion decays.

It was decided that these requirements could be most simply satisfied by a mass spectrometer of the R.F. linear accelerator type, as described by Boyd and Morris (1955). It is difficult to avoid disturbance of the plasma by the stray magnetic field of magnetic deflection type without introducing further complications. This type of radio-frequency linear accelerator mass spectrometer can be made to have a short ion path length which eases the problem of maintaining a good enough vacuum within the mass spectrometer to avoid losses due to collisions.

A block diagram of the mass spectrometer is shown in diagram 3. Ions enter the mass spectrometer through a small orifice by diffusion, and directly behind the orifice is a grid - the injector grid - which is maintained at a high accelerating potential with respect to the orifice. The ions are thus accelerated to a velocity large compared with their initial thermal velocities and also they are focused into a beam. Each ion species will then have a velocity which has a magnitude inversely proportional to its charge to mass ratio. The ions then enter the analyser which consists of a series of short metal tubes arranged in line with alternate tubes electrically connected. An alternating voltage of variable frequency is applied between the two sets of tubes so that a miniature linear accelerator is formed which with one particular applied frequency will accelerate ions of one particular charge to mass ratio. If all the tubes are of equal length the energy gained by a tuned ion must be small compared with the injection energy, otherwise an ion will not remain in tune as it travels down the analyser. On leaving the analyser the ions pass through a grid and enter a retarding field which is of such a

DIAGRAM 2 : CROSS SECTION OF MASS SPECTROMETER

ORIFICE DISC
INJECTOR GRID
MICA WASHER
FRONT END SUPPORT
PRECISION BORE TUBE

CARRIER TUBE

ANALYSER SUPPORT RODS

DRIFT SPACE

CONNECTION TO CIRCULATION PUMP

REAR END SUPPORT

FIRST RETARDER GRID

SECOND RETARDER GRID

COLLECTOR CUP

FOR CLARITY CERTAIN PARTS ARE NOT SECTIONED ON THE HORIZONTAL AXIS

SCALE: APR 1½ = FULL SIZE

magnitude that only those ions which have been accelerated in the
analyser can reach the collector. The resolving power is a func-
tion of the retarding voltage, for it is possible to obtain high
resolving power at the expense of a poor current efficiency if the
retarding potential is set close to the potential equivalent to the
maximum energy gained by the tuned ions in the analyser.

The maximum resolving power obtainable from this type of instru-
ment at a usable current efficiency increases as the number of
stages in the analyser is increased, and a large number of stages
also improves the rejection of harmonically tuned ions. The
maximum resolving power obtainable is also very much dependent
on the stability of the various electrode potentials. These points
have been fully dealt with by Kerr (1956).

3.3.1 The Mass Spectrometer Mechanical Structure

It was decided from the results obtained in previous work with a
mass spectrometer of this type, built by L. W. Kerr (1953), that
a 24-stage analyser would give adequate resolving power. The
maximum practical value of injection potential which can be used
is of the order of 600 volts, as higher voltage results in awkward
insulation problems. The maximum practical frequency which
can be applied to the analyser is about 60 Mc/s since at higher
frequencies difficulties associated with stray capacities and the
amplitude stabilisation of the oscillator become too great. If
protons are to tune at 60 Mc/s with 600 volt injection , an analyser
stage length of 2.85 mm. is required giving an overall analyser
length of 68 mm. The mechanical difficulties associated with the

construction of such an accelerator which would be mechanically
rigid and yet not cause a large obstruction of the gas flow are
great. The analyser was, therefore, made in two sections of
eight stages each, separated by a drift space equivalent in
length to seven stages : this arrangement gives the effective
resolving power of a 24-stage analyser with the harmonic rejec-
tion of a 16-stage instrument. This makes it possible to pump
the mass spectrometer from its centre rather than from one end
which considerably improves the gas flow to the pump. It has
been found that the minimum practical R.F. voltage which can be
applied to the analyser is approximately 5 volts r.m.s. which
means that the tuned ion maximum energy gain (112 eV.) is not
negligible compared with the injection energy (600 eV.). To
compensate for this, the analyser was constructed with stages
which increased progressively in length in the direction in which
the ions travel, the last stage being approximately 10% longer
than the first stage.

A further factor which affects the maximum attainable resolving
power is the efficiency of the retarder-collector assembly. It
has been pointed out by Kerr (1956) that in order to obtain
optimum current efficiency and resolving power the collector
should ideally accept all ions having an energy above a pre-
determined level and reject all others. This implies that the
lines of forces in the retarding field must be accurately parallel
to the axis of the ion beam over the volume occupied by the beam.
This retarding field is, therefore, applied between two accurately
parallel grids in which the wires are as fine as possible.

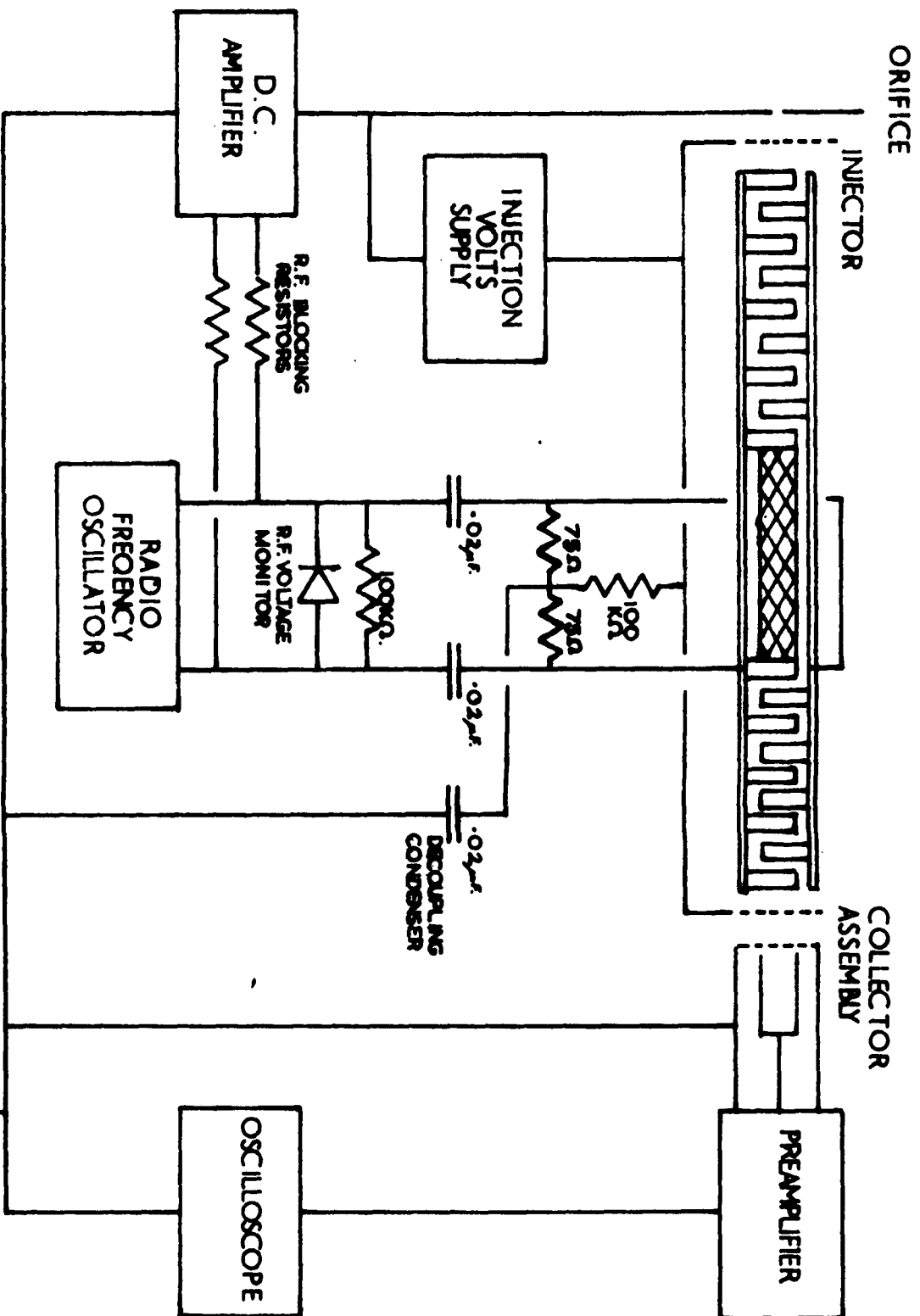A sectional drawing of the mass spectrometer is shown in

DIAGRAM 3 BLOCK DIAGRAM OF SPECTROMETER CONTROL EQUIPMENT

diagram 2. The Nilo-K orifice disc, which is 0.020 inch thick,
is sealed into the end of the precision bore glass tube which
serves to locate the mass spectrometer. A .008 inch diameter
orifice was pierced in the centre of the disc after the seal had
been made and it was necessary to etch down the centre portion
of the disc to a thickness of 0.005 inch before this could be done
satisfactorily. The whole piercing operating was carried out in
a jig to ensure that the orifice would be on the axis of the
precision bore tube. The injector grid is a commercial product
of a type used in microwave triodes with 0.0005 inch diameter
tungsten wires gold brazed on to a molybdenum former at a spacing
of 0.003 inch. In order to protect the gold from attack by mercury
the grids were plated with a thin coating of nickel before they were
spot welded to their mounts.

The analyser tubes were made from strips of Nilo-K, each strip
being initially milled to approximately the correct width. The
strips were then bent to the correct shape and the tubes so formed
finally ground by hand to the correct length. The tubes were
assembled on a jig, the spacing between them being constant, and
each tube was spot welded to its appropriate support rod. The
drift space was enclosed with a fine nickel gauze to screen the
ion beam from possible wall charging effects. The two support
rods were then glass sealed into their end supports. These end
supports were bolted to the Nilo-K tube which forms the carrier
for all these components. The carrier tube was turned on its
outside diameter so as to be a good fit in the precision bore glass
tube and a large part of its centre portion was cut away to provide
a large pumping aperture. This whole arrangement was stress

relieved at 500° C, while it was still in the jig in order to prevent
distortion occurring during making. The injection grid was spot
welded directly to the front end support, while the first retarder
grid - of identical construction - was mounted on a plate bolted
over the rear end support. The carrier tube was insulated from
the orifice disc by means of a mica washer. The second retarder
grid is at earth potential and forms part of the screen round the
collector. The collector itself is a Nilo-K cup which was glass
sealed into a block which forms its screen and also the support
for the second retarder grid. This block is carried on four
rods screwed into the analyser carrier tube and insulation was
obtained by means of pyrophillite bushes and washers. Care
was taken here to ensure that the two retarder grids were as
close to parallel as possible.

The electrical connections to the mass spectrometer, apart from
the one to the orifice, were brought out of the vacuum system
via a commercial sintered glass base. This base contained a
coaxial lead which enabled the ion collector lead to be completely
screened right through to the amplifier. The orifice lead was
brought out through a glass to metal seal through the wall of
the discharge vessel.

3.3.2 The Mass Spectrometer Control Equipment

In order to operate the mass spectrometer it is necessary to
supply the electrodes with certain stabilised voltages and also to
amplify the ion current reaching the collector. The electronic

equipment necessary to do this was built up as two units - the
ion current preamplifier and the mass spectrometer voltage
supply unit.

a) The Ion Current Preamplifier

This amplifier is required to amplify the ion currents reaching
the collector during the afterglow period, without being paralysed
by the much larger current occurring during the discharge pulse
period. Experience with an earlier mass spectrometer of the
same type has suggested that a high frequency limit of 1 Mc/s
would be adequate for this preamplifier, as the shape of the
trailing edge of the ionising pulse will not allow very fast ion
decays to be studied. The preamplifier must also pass 50 C/s
the pulse repetition frequency without appreciable attenuation.

The ion current is fed to a load resistor, one end of which is
earthed, and the voltage developed across this resistor is
amplified. The capacitance of the mass spectrometer collector
system, together with its screened connection to the amplifier,
limits the maximum value of load resistor to 10^5 ohm if 1
Mc/s bandwidth is to be maintained. The ion currents obtained
are of the order of 10^{-9} amps which will develop 100 microvolts
across a 10^5 ohm resistor. The Johnson noise in a 'cracked
carbon' resistor of this value is of the order of 40 microvolts
at 1 Mc/s bandwidth, so that it is important that the amplifier
produced as little further noise as possible. A better signal
to noise ratio can be obtained by using a higher load resistor,
but only at the expense of bandwidth. Again, in previous work

with a similar mass spectrometer it was observed that the
preamplifier used was often paralysed by the positive ion pulse
during the discharge period. This paralysis was due to the
grid of one of the valves in the amplifier being driven into the
grid current region and causing the valve to cut-off for a period
of time controlled by the time constant of the coupling components.

An investigation was made to find the most suitable amplifier
circuit to fit the above requirements. A number of circuits
using various types of valves under different conditions were
tried for the first stage of the amplifier to find the arrangement
which produced the least noise: a low noise transistor circuit
was also tested. The best signal to noise ratio was obtained
using a special quality double triode valve working in a cascode
circuit. The paralysis problem was overcome by arranging
that all stages, which have positive going signals when the input
pulse is positive, are directly coupled. It was found to be
necessary to couple the cascode amplifier to the following stage
by means of a cathode follower, in order to maintain adequate
voltage gain at the required bandwidth. This cathode follower
is A.C. coupled to a 'D.C. ring of three' circuit having a gain
of 20, the feedback across this part of the circuit helping to
stabilise the gain and improve linearity. The final stage is a
high current cathode follower to drive the high input capacitance
of the oscilloscope being used. It is important that there should
be a negligible amount of hum on the amplifier output, as the
pulse equipment is run synchronised to the mains. In order to
accomplish this a stabilised power pack was designed to supply
both the H.T. voltage and heater voltage. The heater supply

is an all transistor D.C. stabiliser which on test gave 0.4 mv,
ripple at full load and the H.T. supply is a standard series
stabiliser circuit which on test gave a maximum of 0.4 mv.
ripple.

Filters are included both in the mains supply lead to the power
pack and in the lead joining the power pack to the amplifier to
exclude R.F. pick-up from the pulse power oscillator. It was
necessary to doubly screen the amplifier iself for the same
reason. The frequency response of the complete amplifier is
3 db down at 700 Kc/s and the noise referred to the input, exclu-
ding that introduced by the load resistor, is 16 microvolts. It
is arranged so that the load resistor can be liquid air cooled,
which gives an improvement in signal to noise ratio by a factor
of two when maximum sensitivity is required.

b. The Mass Spectrometer Voltage Supply Unit

Three separate electrode potentials are necessary to operate the
mass spectrometer, the injection voltage, the retarding voltage
and the R.F. voltage which is applied to the analyser. It is
necessary that the two D.C. potentials are independently revers-
ible so that the positive or negative ions may be studied. The
maximum resolving power attainable with the mass spectrometer
is very much dependent on the stability of these potentials : this
has been discussed fully by Kerr (1956). In order to ensure that
the resolving power was not in fact limited by the control
equipment, it was designed to give 1% resolving power with a

perfect mass spectrometer. A suitable general design for this
equipment was developed for previous work, and it was slightly
modified to make it suitable for use with the present ma ss
spectrometer.

The most difficult problem to overcome is the maintainance of a
constant amplitude of radio-frequency voltage on the analyser,
as the oscillator frequency is varied. When high resolution is
required from the mass spectrometer, it is necessary to set
the retarding voltage close to the voltage corresponding to the
maximum energy gained by the tuned ions in the analyser. In
these conditions even a small variation in the amplitude of the
R.F. voltage will cause the current efficiency to vary widely,
and hence good resolution cannot be obtained. In practice, the
amplitude of the R.F. voltage on the analyser cannot be simply
stabilised to better than about 5% and it may be shown from the
work of Kerr (1956) that this corresponds to a mass resolving
power of approximately 10% if the retarding voltage does not
vary. However, it is the ratio of the R.F. voltage on the
analyser to the retarding voltage which controls the resolving
power, and the problem can be overcome if this ratio is kept
constant. This is done by monitoring the R.F. voltage on the
analyser with a diode and amplifying t he resultant D.C. vol-
tage to obtain the retarding voltage. A resolving power of 1%
can then be obtained, despite there being small variations in
the amplitude of the R.F. voltage, provided that the monitor-
ing and D.C. amplifying equipment has a gain and zero stability
of better than 0.2%. The stability of the other electrode
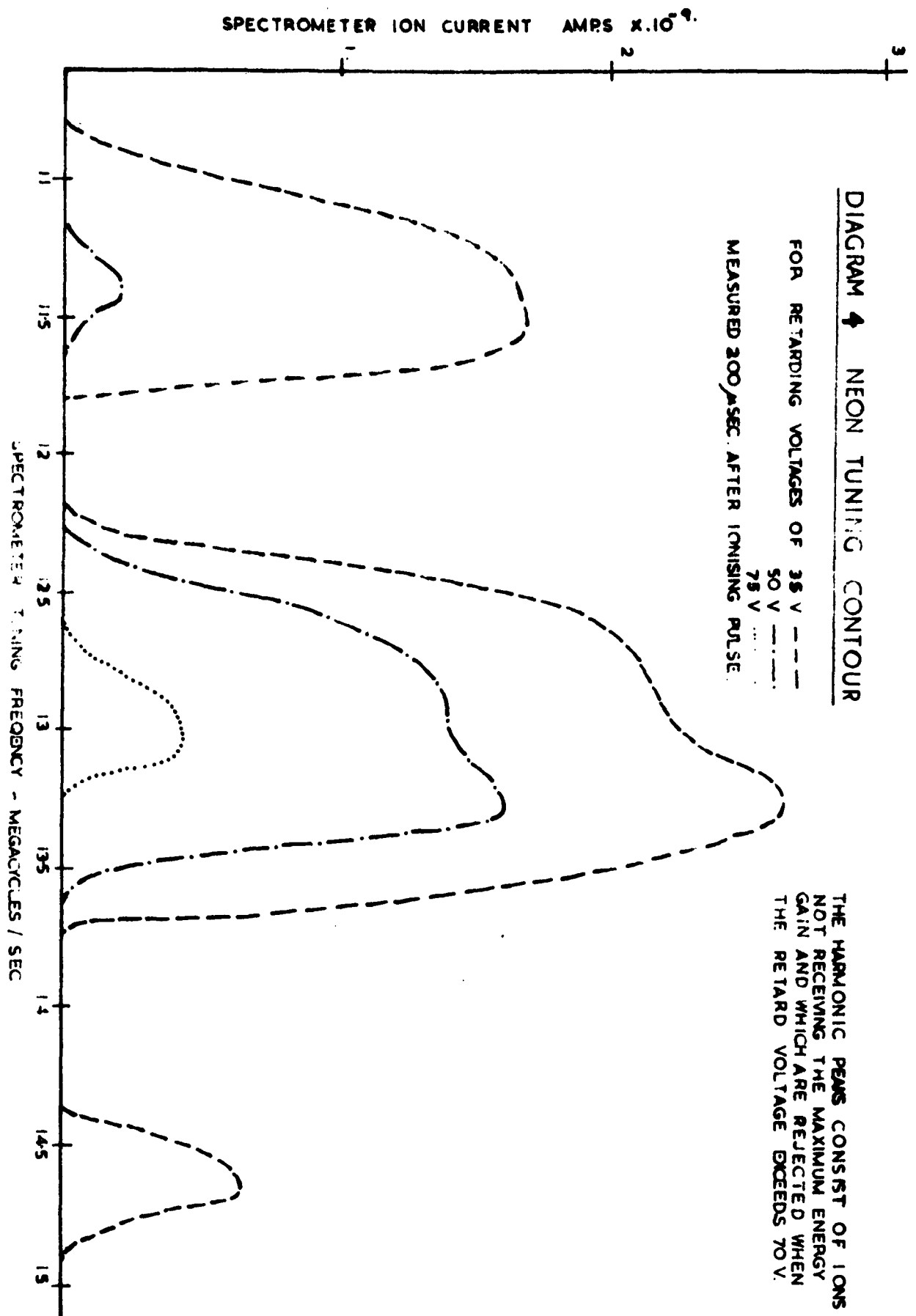potentials also enter into the problem and to achieve 1%

resolving power the injection voltage must be stable to better than 0.5% during the time taken to complete any one measurement. The long term stability of these two supplies affects the accuracy of the mass calibration, and when very accurate determination of mass is required an external substandard voltmeter and a wave-meter may be used. The equipment was built to the above specifications and performs according to design. The oscillator covers a frequency range from 3.6 to 75 Mc/s in six ranges which enables all singly charged ions of mass less than 264 a.m.u. (Cs_2^+) to be studied.

A crystal frequency calibration arrangement is built into the oscillator: the retarding voltage is continuously variable over a range from zero to a value corresponding to the maximum energy gained by the tuned ions. This enables the resolving power and current efficiency to be varied to suit the experimental conditions. A block diagram of the complete control equipment is shown in Diagram 3.

4. Performance of the Mass Spectrometer

An approximate value of the mass resolution of the spectrometer was calculated, but the complex computation required to produce a more exact value was not undertaken. Trial measurements were made therefore in a pure neon discharge to test and assess the performance of the mass spectrometer.

A 0.4 mm. Hg. pressure neon discharge, of relatively low initial

DIAGRAM 4 NEON TUNING CONTOUR

FOR RETARDING VOLTAGES OF 35 V — — —
50 V — · — · —
75 V · · · · · ·

MEASURED 200 μSEC. AFTER IONISING PULSE.

SPECTROMETER ION CURRENT AMPS X. 10⁻⁹

SPECTROMETER TUNING FREQUENCY ~ MEGACYCLES / SEC

THE HARMONIC PEAKS CONSIST OF IONS NOT RECEIVING THE MAXIMUM ENERGY GAIN AND WHICH ARE REJECTED WHEN THE RETARD VOLTAGE EXCEEDS 70 V.

ion density - an estimated 10^9 ions /cc - created a spectrometer
current of 10^{-8} A when no retarding volts were applied, and even
at high resolution the current of 4×10^{-10} A was well above the
amplifier noise level. These ion currents were obtained with the
orifice plate connected to the plasma reference electrodes, and
an improvement could be made in the ion current if the potential
of the orifice were altered with respect to the reference elec-
trodes. However, no investigation has yet been made of the effect
of the resulting electric field on the afterglow conditions.

The tuning frequency ion current graph is shown in diagram 4
for a typical neon discharge of 0.4 mm. Hg. pressure. When low
retarding potentials were used, harmonic peaks were observed at
tuning frequencies of 0.85 and 1.11 times the central peak frequency.
These harmonics vanished as the retarding potential is raised above
about 65% of the value, equivalent to the maximum energy gain of
the tuned ions : the current efficiency of these conditions, however,
was still satisfactory.

The size of the lower frequency harmonic peak is unexpectedly
large, and it is thought that the geometry of an accelerator section,
a drift space and a second accelerator section in the mass spectrom-
eter tends to favour the passage of ions when the applied tuning
frequency is below the centre peak frequency.

A complete analysis of this effect has not yet been worked out. The
asymmetry of the neon peak is unique among the ion peaks observed,
and possibly represents the contribution of the ion of the isotope
Ne_{22}, but this asymmetry is greater than would be accounted for by
the isotopic abundance of Ne_{22} (0.0%). The absolute identification of

DIAGRAM 5. TUNING CONTOUR IN A NITROGEN AFTERGLOW

RETARDING VOLTAGE 7·5 VOLTS
MEASURED 200 μSEC. AFTER IONISING PULSE

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SPECTROMETER TUNING FREQENCY. MEGACYCLES /SEC.
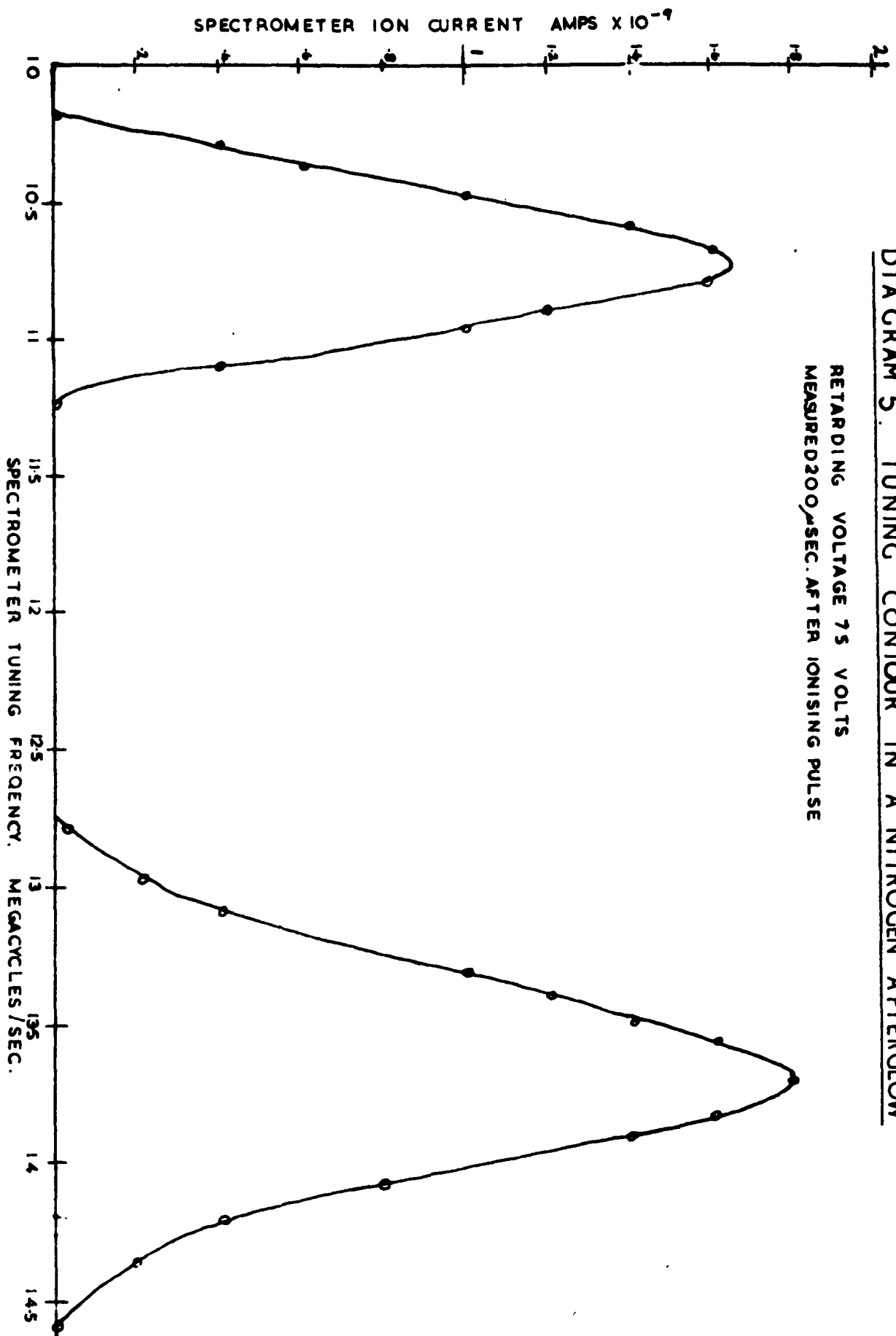
this ion was not possible as an uncertainty existed due to a fault in the injection voltage measuring system and an exact calibration of this supply is being carried out to remove the anomaly.

The neon discharge was otherwise as expected except that a very small atomic hydrogen ion current was just detectable, the magnitude being about 1/30 that of the neon ion current. This impurity may have been derived from water present in the yet unbaked system.

The best measured resolving power of the instrument at the present time is 5%, which is sufficient to resolve masses 28, 30 and 32, this being one of the design criteria.

In nitrogen discharges at about 0.8 mm. Hg. pressure, two peaks were observed - see diagram 5. The resolving power is in agreement with that of the neon peak, while the theoretical masses represented are 28.2 a.m.u. and 17.2 a.m.u. The former is probably N_2^+ and the latter either NH_3^+ or OH^+, both of which have been observed in previous work in nitrogen by the authors. Tests in a lower pressure (0.06 mm. Hg.) nitrogen afterglow show that the atomic nitrogen ion N^+ is present, otherwise no further ions could be detected. It may be seen that these peaks are not asymmetrical, suggesting that the asymmetry of the neon peak is not an instrumental effect. Prior to making further measurements, the system will be thoroughly baked and another check on impurities will be carried out.

This work is being actively continued and now that the apparatus has been completed it is hoped that it will be possible to publish technical scientific notes on the measurement of certain reaction cross-sections in the near future.

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A laboratory method is outlined for studying some of the low energy ionic reactions that are likely to occur when easily ionisable chemicals are released into the ionosphere. The possibility of resolving some of the discrepancies in previous measurements of relevant cross-sections is discussed. The design of apparatus to make measurements in afterglows using a time resolving mass spectrometer and a Langmuir probe is described, and the construction and initial measurements of performance of the mass spectrometer are given in detail.